

Ambient Volatility of DMMP

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Key Words: Vapor-Liquid Equilibrium, Mixture, Data, Experimental,
Dimethyl Methylphosphonate, Water

Abstract

A novel experimental apparatus and procedures have been developed and implemented to measure the volatility of a chemical warfare agent simulant as a function of ambient temperature and water vapor partial pressure. Initial data have been measured for dimethyl methylphosphonate (DMMP) to validate the methodology. The results presented herein reveal a significant volatility suppression for DMMP, increasing as relative humidity increases. Deviation from ideal behavior as described by Raoult's Law has been quantified. The maximum deviation from ideality occurs at water partial pressures near 500 pascals. An empirical model has been developed to enable interpolation and limited extrapolation of the data to higher water partial pressures as might be found in compressed-air regenerative filtration applications.

Introduction

The vapor pressures of dimethyl methylphosphonate (DMMP)¹ and a number of chemical warfare agents, e.g., O-ethyl-2-(isopropylaminoethyl)methyl phosphonothiolate (VX)^{2,3} and cyclohexyl methylphosphonofluoridate (GF)⁴, have been measured in the ambient temperature range recently. So far, that work has not included effects of atmospheric water vapor. The objective of studying the volatility of toxic vapors in humid environments is to refine predictions of downwind time-concentration evolution following deposition of chemicals into the environment as well as to determine more realistic environmental evaporation rates, i.e., persistence. The work reported here establishes methodology to characterize materials of interest.

Experimental

Figure 1 shows schematically the experimental set-up used in the present work. Two vapor saturators [1] were used in parallel, and their effluent streams were combined in a heat-traced Nalgene 890 pTFE FEP 1/4-inch tubing (3/16-inch i.d.) transfer line. The combined vapors were then passed through a mixing cell, ca. 25 cubic centimeters. A portion of the mixing cell effluent was drawn into a chilled mirror dew pointer (Model 911 Dew-All™ Digital Humidity Analyzer, EG&G Environmental Equipment, Burlington, MA), and the dew point temperature was measured and recorded.

Data acquisition was performed using National Instruments LabView® software and interfaces (SCXI 1001 chassis equipped with various 1320-series modules). Controlled parameters included the temperatures of both saturator baths, mixing cell temperature, ambient temperature, and saturator flow rates. Measured data included the mixture dew point temperature, saturator flow rates and bath temperatures, ambient pressure, and GC traces with integrated DMMP area. All of the data were captured and stored by the control program. This afforded the opportunity to change operating parameters on the fly and conduct unattended operations.

99% DMMP was obtained from Alfa Johnson Matthey (Ward Hill, MA) and used without purification. Distilled water was used to generate water vapor.

The first series of experiments used flow rates of 250 sccm for the water saturator and 50 sccm for DMMP saturator to simulate high-humidity conditions. The second series used flows of 100 and 200 sccm, respectively, to explore low-humidity conditions.

Experimental Schematic

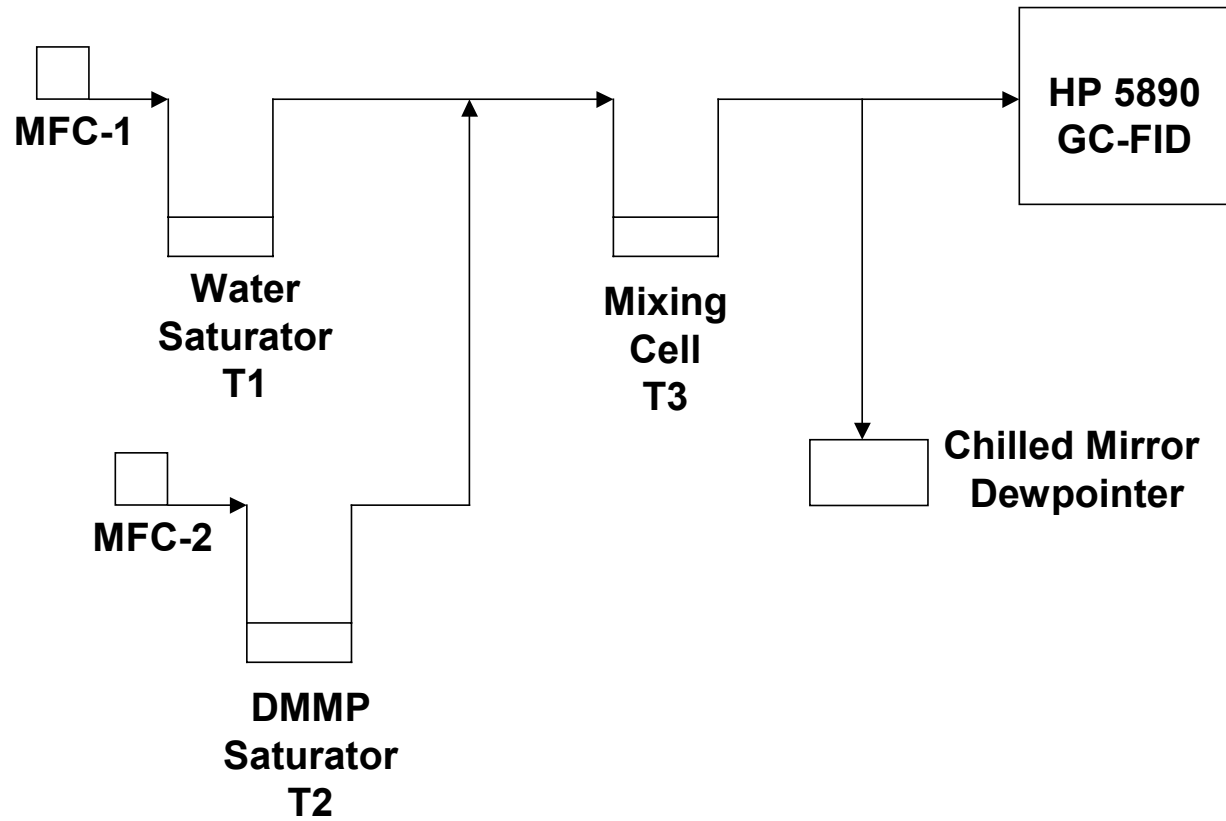


Figure 1. Experimental Diagram

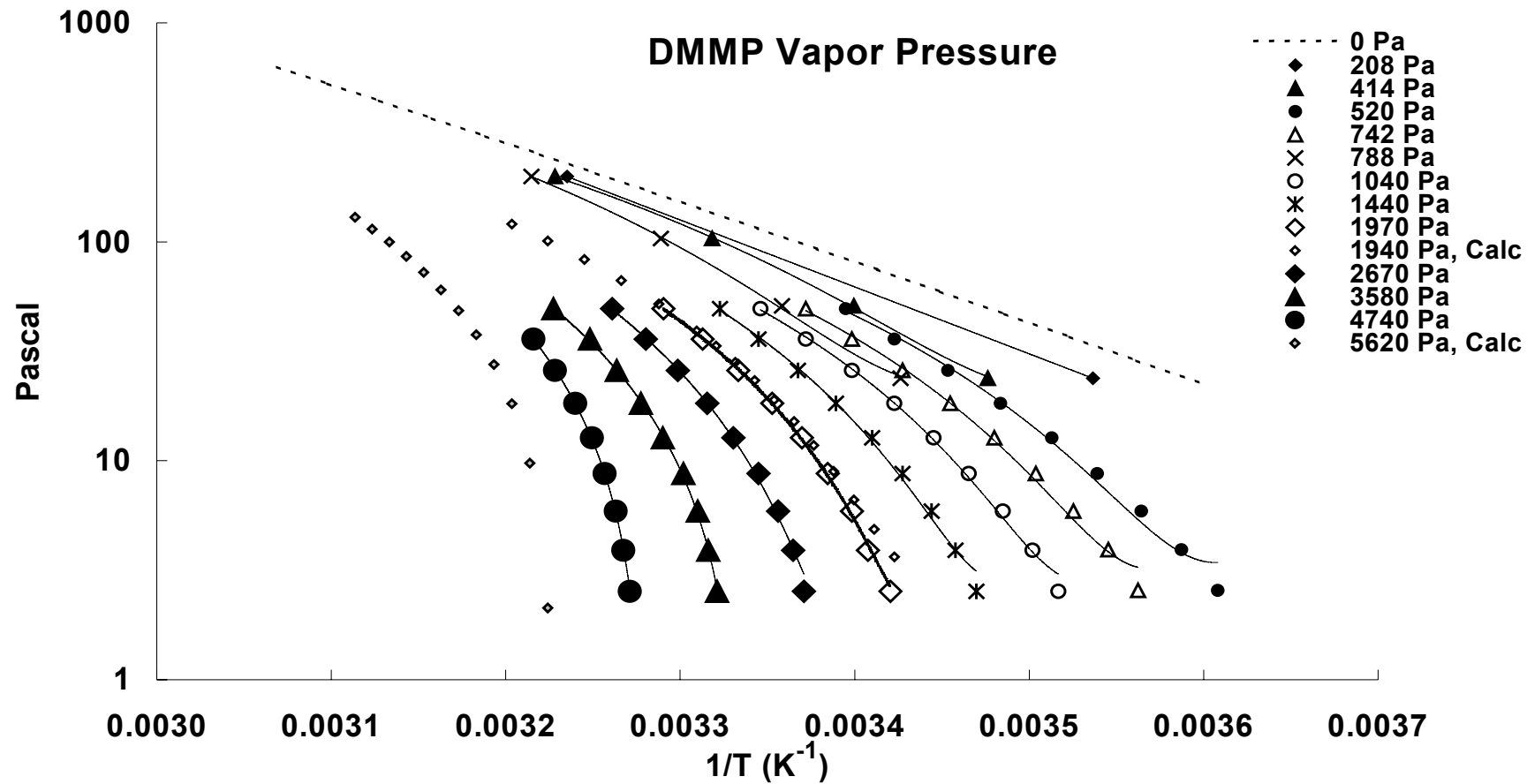


Figure 2. Measured vapor pressure of DMMP as a function of temperature at several water partial pressures. Lines indicate quadratic fits to data points. Small diamonds are calculated based on quadratic fits.

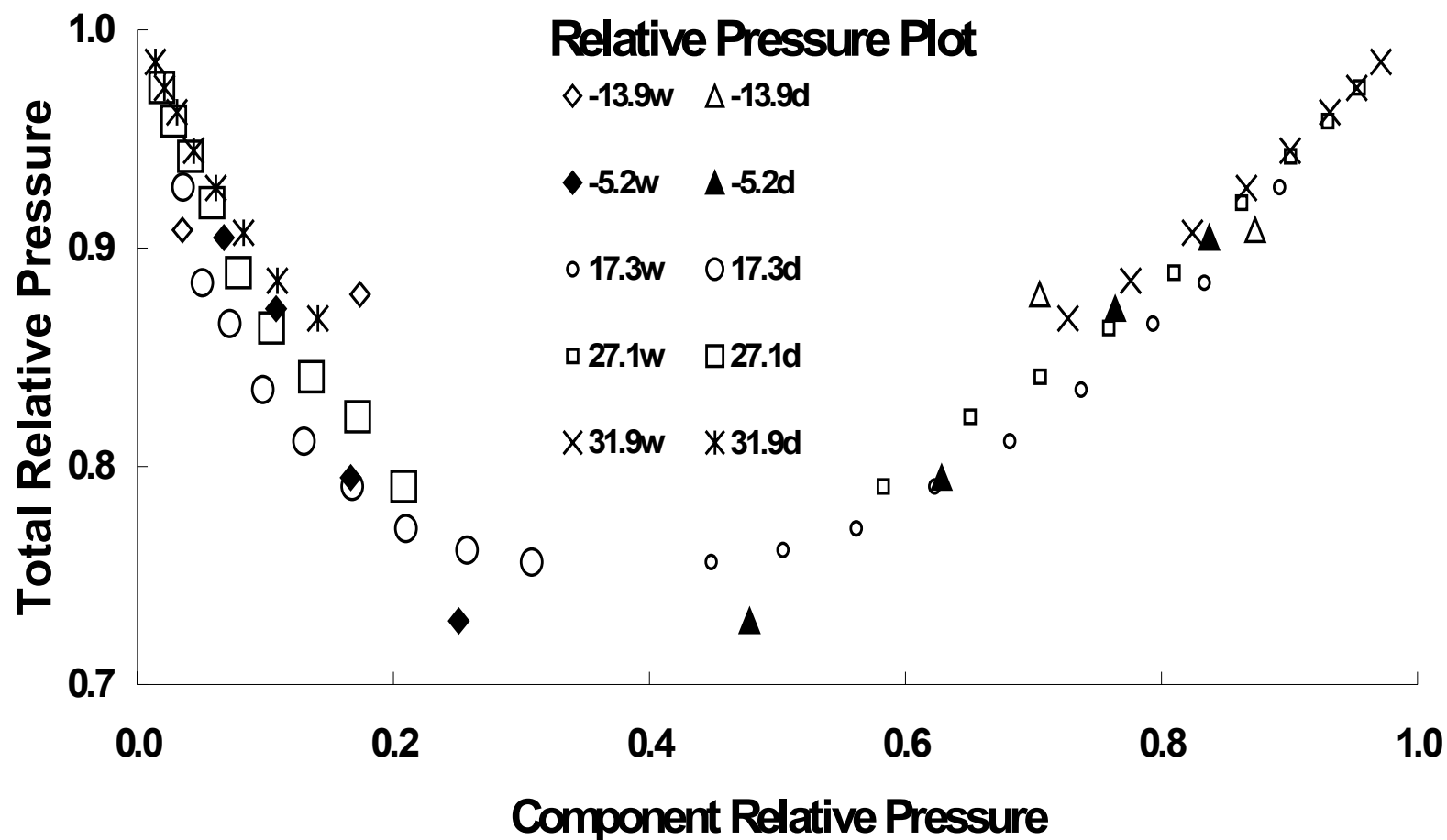


Figure 3. Sum of relative pressures of DMMP and Water vs. component relative pressures. Open diamonds (-13.9w) represent water relative pressure (RH) at a Water dew point of -13.9°C , open triangles (-13.9d) represent DMMP Relative pressure at a Water dew point of -13.9°C , etc.

Results

Table 1 shows the measured dew points and the partial pressure of each component in the mixture from series 1 in this study. Table 2 lists similar data for series 2. Figure 2 shows a plot of the measured volatility of DMMP as a function of temperature at 11 different water partial pressures investigated in the present work, as well as vapor pressure data previously measured for DMMP using ultra-dry conditions¹, and calculations for two humidity series not measured in this work are also shown.

Figure 3 shows a plot of the sum of the relative pressures of the components (DMMP plus water) versus the relative pressure of each component for three data sets from series 1 and two data sets from series 2 that span the range of water partial pressures investigated in this work. The trend shown in figure 3 clearly illustrates a deviation from Raoult's Law and will be discussed below in more detail, however, it should be noted at this point that there are six other data sets similar to the five presented here. The other data are consistent with those shown in Figure 3 and reveal clear trends, i.e., the magnitude of the deviation from Raoult's Law reaches a maximum near water partial pressure values near 500 Pascal.

| P(H₂O) Pascal | 520 | 742 | 1040 | 1440 | 1970 | 2670 | 3580 | 4740 |
|---------------------------------|------------------------|------------|-------------|-------------|-------------|-------------|-------------|-------------|
| P(DMMP) Pascal | Mixture Dew Point (°C) | | | | | | | |
| 2.6 | 4.0 | 7.55 | 11.2 | 15.05 | 19.2 | 23.5 | 27.95 | 32.55 |
| 3.9 | 5.6 | 8.9 | 12.4 | 16.05 | 20.3 | 24.05 | 28.4 | 32.9 |
| 5.9 | 7.4 | 10.5 | 13.8 | 17.2 | 21.1 | 24.8 | 28.95 | 33.3 |
| 8.7 | 9.4 | 12.25 | 15.4 | 18.6 | 22.3 | 25.8 | 29.7 | 33.9 |
| 12.7 | 11.5 | 14.2 | 17.1 | 20.1 | 23.6 | 27.1 | 30.8 | 34.6 |
| 18.3 | 13.9 | 16.3 | 19 | 21.9 | 25.1 | 28.45 | 31.95 | 35.5 |
| 25.8 | 16.4 | 18.6 | 21.1 | 23.8 | 26.85 | 30 | 33.25 | 36.6 |
| 36.0 | 19 | 21.1 | 23.4 | 25.8 | 28.7 | 31.7 | 34.7 | 37.8 |
| 49.6 | 21.4 | 23.6 | 25.7 | 27.8 | 30.75 | 33.5 | 36.7 | |

Table 1. Measured mixture dew points at indicated DMMP and **water vapor** partial pressures from series 1, water vapor flow = 250 sccm and DMMP flow = 50 sccm.

| P(H₂O) Pascal | 208 | 414 | 788 |
|---------------------------------|------------------------|------------|------------|
| P(DMMP) Pascal | Mixture Dew Point (°C) | | |
| 23.8 | 9.6 | 14.5 | 18.7 |
| 51.1 | | 21.0 | 24.6 |
| 103.6 | | 28.2 | 30.9 |
| 198.8 | 35.9 | 36.6 | 37.9 |

Table 2. Measured mixture dew points at indicated DMMP and **water vapor** partial pressures from series 2, water vapor flow = 100 sccm and DMMP flow = 200 sccm.

Discussion

Raoult's Law states that the partial pressure of components over an ideal liquid mixture is given by the product of the pure component vapor pressure and mole fraction (x) for each component:

$$\begin{aligned} P_1 &= x_1 \cdot (P_1)^0 \\ P_2 &= x_2 \cdot (P_2)^0 \\ &\text{etc.} \end{aligned}$$

This expression is usually applied to the liquid phase in order to estimate the vapor phase composition and is commonly used to model purification of liquids by distillation. An identical expression of Raoult's Law for a two-component mixture is:

$$\begin{aligned} x_1 &= P_1/(P_1)^0 \\ x_2 &= P_2/(P_2)^0 \end{aligned}$$

where $P_1/(P_1)^0$ represents the relative pressure of component #1, and $P_2/(P_2)^0$ represents the relative pressure of component #2. (For water, relative pressure is commonly referred to as relative humidity). By employing material balance, the sum of the relative pressures over an ideal solution will always equal unity. Conversely, the partial pressure of vapor component #2 at a particular condition is predictably altered (suppressed) by the presence of component #1. As shown in Figure 3, the sum of the partial pressures is significantly less than 1.0, and the deviation from ideal behavior maximizes at RH values near 40%. The observed deviations from Raoult's Law are greatest at water partial pressures near 500 Pa. Most likely, intermolecular interactions, i.e., intermolecular hydrogen bonding between water and DMMP, play a role in causing the non-ideal behavior, and work is ongoing to investigate this phenomenon theoretically and by infrared spectroscopy⁵.

Modeling

A quadratic equation correlation between the measured mixture dew point temperatures and DMMP partial pressure was developed for data measured at each water partial pressure with the exception of the data measured at a water partial pressure of 208 Pascal. These equations are listed in Table 3.

| Water Partial Pressure (Pa) | DMMP Vapor Pressure Correlation (Pa) |
|-----------------------------|---|
| 414 | $P_{\text{DMMP}} = 2.15\text{E}+09/T^2 - 1.51\text{E}+07/T + 2.66\text{E}+04$ |
| 520 | $P_{\text{DMMP}} = 9.99\text{E}+08/T^2 - 7.20\text{E}+06/T + 1.30\text{E}+04$ |
| 742 | $P_{\text{DMMP}} = 1.17\text{E}+09/T^2 - 8.38\text{E}+06/T + 1.50\text{E}+04$ |
| 788 | $P_{\text{DMMP}} = 3.16\text{E}+09/T^2 - 2.18\text{E}+07/T + 3.77\text{E}+04$ |
| 1040 | $P_{\text{DMMP}} = 1.38\text{E}+09/T^2 - 9.74\text{E}+06/T + 1.72\text{E}+04$ |
| 1440 | $P_{\text{DMMP}} = 1.81\text{E}+09/T^2 - 1.26\text{E}+07/T + 2.20\text{E}+04$ |
| 1970 | $P_{\text{DMMP}} = 2.07\text{E}+09/T^2 - 1.42\text{E}+07/T + 2.45\text{E}+04$ |
| 2670 | $P_{\text{DMMP}} = 2.62\text{E}+09/T^2 - 1.78\text{E}+07/T + 3.02\text{E}+04$ |
| 3580 | $P_{\text{DMMP}} = 2.69\text{E}+09/T^2 - 1.81\text{E}+07/T + 3.05\text{E}+04$ |
| 4740 | $P_{\text{DMMP}} = 4.27\text{E}+09/T^2 - 2.83\text{E}+07/T + 4.69\text{E}+04$ |

Table 3. Quadratic Equations Describing the Vapor Pressure of DMMP at Several Water Vapor Partial Pressures. (T = °K).

The equations fit the data quite well as shown by the lines connecting the data points in Figure 2, although the quality of the fits falls off at lower temperatures for several of the lower water partial pressure curves.

A more general predictive capability was derived by correlating the coefficients of these equations to the water dew point temperatures. Two predicted DMMP vapor pressure curves based on these correlations are shown in Figure 2 for water partial pressures of 1940 and 5620 Pa. The former compares well with data measured for water partial pressures of 1970 Pa; the points are slightly higher than the measured data as expected by the trend of decreasing DMMP vapor pressure as the water partial pressure increases. The latter (water partial pressure = 5620 Pa) also seems to predict what might be expected for a water dew point of 35°C as well as the trend of changing shapes of the lower water partial pressure data.

It is instructive to note that the present data, when plotted using standard vapor pressure format (figure 2), are very non-linear. The deviation from linearity increases as the water partial pressure increases. Two limits dictate the observed non-linearity. At low water relative pressures, each two-component vapor pressure curve approaches the line representing the dry DMMP vapor pressure line (upper left of figure 2). At low DMMP partial pressures for each two-component vapor pressure curve, the lines asymptotically approach the vertical line defined by the water dew point of that series.

The heat of vaporization can be inferred from volatility data using standard methods. Using the Antoine equation, $\ln(P) = a - b/(c+T)$,

$$\Delta H_{\text{vap}} = bRT^2/(c+T)^2$$

In this case, the *apparent* ΔH_{vap} varies from that of single-component DMMP (ca. 50 kJ/mol) at low RH values to unrealistically high values (>350 kJ/mole) at high humidity conditions.

Conclusions

The present data demonstrate clearly that the volatility of DMMP is very sensitive to the presence of water vapor as well as temperature. In addition to the expected suppression described by Raoult's Law, a significant negative deviation from ideal behavior has been observed. The results of the present work enable accurate predictions of the evaporation of DMMP in the environment at a wide variety of temperature and dew point conditions. A simplistic model has been developed from the present data that would allow prediction of DMMP volatility at any atmospheric relative humidity condition. The model could be extended to higher humidity values characteristic of industrial processes or, of more immediate interest, feed conditions for air purification systems employing high temperature and pressure, such as pressure-swing adsorption, where influent water partial pressure may be exceed 10^4 Pascal and ambient temperatures may exceed 50°C.

Figure Captions

Figure 1. Experimental Schematic

Figure 2. Measured vapor pressure of DMMP as a function of temperature at several water partial pressures. lines indicate quadratic fits to data points. small diamonds are calculated based on quadratic fits.

Figure 3. Sum of relative pressures of DMMP and water vs. component relative pressures. open diamonds (-13.9w) represent water relative pressure (RH) at a water dew point of -13.9°C , open triangles (-13.9d) represent DMMP relative pressure at a water dew point of -13.9°C , etc.

Acknowledgments

The authors wish to thank Dr. Frank Verderame and Prof. Fred Longo for helpful discussions and Mr. Ed Weller for technical assistance.

References

1. Tevault, D.E., Keller, J., and Parsons, J., "Vapor Pressure of Dimethyl Methylphosphonate", Proceedings of the 1998 ERDEC Scientific Conference on Chemical and Biological Defense Research, ECBC-SP-004, pp. 815-822, July 1999. Unclassified Special Report.
2. Buchanan, J.H., Buettner, L.C., Butrow, A.B., and Tevault, D.E., "Vapor Pressure of VX", ECBC TR-068, November 1999. Unclassified Technical Report.
3. Rittfeldt, L., "Determination of Vapor Pressure of Low-Volatility Compounds Using a Method to Obtain Saturated Vapor with Coated Capillary Columns," Anal. Chem. 2001, 73, 2405-2411.
4. Tevault, D.E., Buchanan, J.H., Buettner, L.C., and "Vapor Pressure of GF". Unclassified ECBC Technical Report, in press.
5. Ault, B., Balboa, A., and Tevault, D.E., unpublished data.